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(54) Title: OCTANE IMPROVING GASOLINE ADDITIVES		
(57) Abstract <p>The present invention is a method, and the product thereof, to increase the octane index of gasoline through the use of a combination of oxygenated hydrocarbons and organometallic compounds. A gasoline mixture is prepared containing between 75 to 95% unleaded gasoline, 5 to 25% oxygenated hydrocarbons such as alcohols of less than 5 carbons, between about 0.05 g to 4 g Pb/gal. and between about 0.005 g to 0.15 g Mn/gal. The actual percentages of alcohol and organometallic compounds which are added may be optimized as necessary to produce the desired increase in octane using empirical methods similar to the procedures used in the following examples. The preferred alcohol composition consists of between 33 to 100% denatured ethyl alcohol and 0 to 67% methyl alcohol and makes up between 7.5 and 10% by volume of the gasoline mixture. Other oxygenated hydrocarbons of fewer than 5 carbons which can be used in place of or in addition to ethanol and methanol include isomers of propanol and butanol, methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME). Acceptable sources of lead and manganese include organolead compounds such as tetraalkyl lead compounds, especially tetraethyl lead, and derivatives thereof, and organomanganese compounds such as methylcyclopentadienyl manganese tricarbonyl. The preferred quantities of both lead and manganese are in the range of 0.1 mg metal/gallon of gasoline.</p>		

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-1-

OCTANE IMPROVING GASOLINE ADDITIVES

BACKGROUND OF THE INVENTION

The present invention relates to an improved method for the elevation of the octane index of motor gasoline by oxygenated hydrocarbons in combination with organometallic compounds.

5 Oxygenated hydrocarbons such as alcohols and organometallics, in particular tetraethyl lead, have been used to raise the octane index of gasoline for many years. Recently, organomanganese compounds, alone or in combination with organolead compounds, 10 have been used to improve the octane index of gasolines for use in combustion engines. See, for example, U.S. Patent Nos. 4,437,436 to Graiff et al, 390,345 to Somorgai, 4,141,693 to Feldman, et al, 4,140,491 to Allain et al, 4,139,349 to Payne, 15 4,067,699 to Lukasiewicz, 4,040,479 to Dorn, et al, and 4,028,065 and 3,966,429 to Sprague.

Attempts have been made to further increase the octane index by combining oxygenated hydrocarbons and organolead compounds. Unfortunately, when alcohols and 20 lead are blended in the same gasoline mixture, the sum of the increase in octane due to the combined additives is less than the sum of the increase in octane attributable to the lead or the alcohol if added individually to the gasoline. This phenomenon 25 is referred to as the "poor lead susceptibility of alcohol" and is well known to those skilled in the art. Moreover, the higher the starting octane of the base gasoline, the lower the increase in octane attributable to the alcohol.

-2-

There are two major disadvantages to the use of lead in gasoline: lead poisons automobile catalytic converters, thereby reducing the effectiveness of the device in controlling emissions which lead to air pollutants, and lead contained in automotive exhaust causes serious health and learning disorders in those exposed over a period of time to excessive lead quantities. The consumption of leaded gasoline in the United States has declined due to the implementation of clean air standards decreasing the allowable emissions of lead, unburned hydrocarbons, and carbon monoxide. However, since all pre-1975 automobiles and light trucks, most gasoline-powered agricultural equipment, and most recreational vehicles cannot run on gasoline that does not contain at least 0.1 gram of lead per gallon, it is estimated that, as of mid-1987, approximately 25 percent of all gasolines sold in the United States contained lead. In other countries, particularly those in Europe and the third world nations, leaded gasoline is the only type of gasoline utilized.

Due to the reduction in allowable levels of lead in gasoline, considerable pressure has been placed on gasoline refiners to meet the needs of the consumers. A variety of compounds have been added in an attempt to increase the octane index while simultaneously reducing undesirable emissions. For example, the addition of alcohol to unleaded gasoline has been used to significantly reduce the amount of carbon monoxide and unburned hydrocarbons in the exhaust emissions. Alcohol at a level of approximately 10 percent, by volume, has been used in both leaded and unleaded grades of gasoline to increase the octane index and to dilute the more photo-reactive and toxic

-3-

gasoline components. The advantages of the use of alcohol over alternative compounds such as benzene, a known carcinogen, and photo-reactive compounds, such as olefins, are obvious. Unfortunately, as discussed 5 above, the combination of lead and alcohol is not as effective as the use of either alone.

It is therefore an object of the present invention to provide a process and composition using oxygenated hydrocarbons such as alcohols in 10 combination with organometallic compounds to increase the octane index of gasoline.

It is a further object of the invention to provide a method and means for increasing the octane rating of gasoline containing lead while diluting or 15 decreasing the level of unburned hydrocarbons emitted during combustion.

It is a further object of the present invention to provide a method and means for increasing the octane index of a lead-alcohol gasoline mixture, which 20 does not suffer from poor lead susceptibility of the alcohol.

It is a further object of the present invention to provide a method and means for increasing the octane index of gasoline mixtures which provide 25 substantial savings in the cost of the gasoline, both to the refiner and to the end-consumer.

SUMMARY OF THE INVENTION

The present invention is a method, and the product thereof, to increase the octane index of 30 gasoline through the use of a combination of oxygenated hydrocarbons and organometallic compounds. A gasoline mixture is prepared containing between 75

-4-

to 95% unleaded gasoline, 5 to 25% oxygenated hydrocarbons such as alcohols of less than 5 carbons, between about 0.05 g to 4 g Pb/gal and between about 0.005 g to 0.15 g Mn/gal. The actual percentages of 5 oxygenated hydrocarbons and organometallic compounds which are added may be optimized as necessary to produce the desired increase in octane using empirical methods similar to the procedures used in the following examples. The preferred alcohol composition 10 consists of between 33 to 100% denatured ethyl alcohol and 0 to 67% methyl alcohol and makes up between 7.5 and 10% by volume of the gasoline mixture. Other oxygenated hydrocarbons of fewer than 5 carbons which can be used in place of, or in addition to, ethanol 15 and methanol include isomers of propanol and butanol, methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME). Acceptable sources of lead and manganese include organolead compounds such as tetraalkyl lead compounds, especially tetraethyl lead, 20 and derivatives thereof, and organomanganese compounds such as methylcyclopentadienyl manganese tricarbonyl. The preferred quantities of both lead and manganese are in the range of 0.1 mg metal/gallon of gasoline.

DETAILED DESCRIPTION OF THE INVENTION

25 From the foregoing summary, it may be seen that the present invention resides in using a combination of an octane-enhancing blend of alcohols or other oxygenated hydrocarbons and organometallic compounds containing manganese and lead. The manganese, alone 30 or in combination with the lead, acts in combination

with the alcohols to increase the octane index of the gasoline.

The preferred embodiment at the present time is the combination of the oxygenated hydrocarbons, 5 organolead compounds and organomanganese compounds. It may be desirable to provide other additives enhancing performance of the gasoline mixture including carburetor detergents, deposit control agents, fuel intake system cleaners, port fuel 10 injector cleaners, corrosion inhibitors to prevent chemical attack by the oxygenated hydrocarbons on lead and zinc alloys, corrosion inhibitors to prevent conventional rusting by dissolved oxygen in the aqueous phase in the event of a phase separation, and 15 oxidative stabilizers.

The octane index, as referred to herein, is derived by determining the "research octane" value and the "motor octane" value and then determining the average octane value of the two. The research octane 20 is the value derived during combustion of the gasoline under low stress, normal operating temperatures and the motor octane is the value derived during combustion of the gasoline under high stress, pressure and temperature. The procedures for making these 25 measurements are well known to those skilled in the art.

The oxygenated hydrocarbons and organometallic compounds are added to a gasoline base stock. In the most desirable embodiment, a gasoline having the 30 lowest possible octane is utilized since this is the most economical starting material. For example, a gasoline mixture having an effective octane index of between 87 and 89 can be produced according to the present invention from a suitable suboctane gasoline

having an octane index of $(R+M)/2$ in the range of between 83 to 84 (Examples 1 and 2).

Other gasolines and combinations of gasoline and usable refinery blending components may be utilized in 5 the present invention. In another example, an 87 octane unleaded gasoline can be used as the base stock for a mixture containing 10% ethanol, 0.1 g Pb/gal., and 0.1 g Mn/gal. This leaded gasohol has an octane rating of 91.55, far in excess of the 89 octane 10 rating required by most state regulatory agencies for leaded gasohol (Example 3).

Similarly, a blender might mix 90% unleaded gasoline with 10% raffinate to produce a lower octane gasoline base stock. To this new base stock, the 15 blender would then add the alcohol mixture such that the final gasoline meets all of the regulatory specifications and contains 5% methanol, 2.5% ethanol, 0.1 g Pb/gal., 0.1 g Mn/gal., and an additive package consistent with the Du Pont Waiver to the Clean Air 20 Act.

In general, additives should not be blended with the gasoline mixture which would cause the gasoline to exhibit poor performance at the hands of the consumer. For example, the alcohols preferred for use with this 25 invention include methanol, the two isomers of propanol and the four isomers of butanol, all alcohols of fewer than five carbons. These alcohols have been added to gasoline in percentages ranging up to 15% in the U.S. and up to 25% in Brazil without 30 modification of the automobile. In the U.S., the Environmental Protection Agency now limits the amount of total alcohol in gasoline to a maximum of 10%. Other oxygenated hydrocarbons beside alcohols which have been used in motor gasolines to improve octane

-7-

and reduce exhaust emissions include methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME).

A number of products can be used to deliver 5 elemental lead to the combustion mixture. These are commonly referred to as tetraethyl lead (TEL), and are generally mixtures of tetraalkyl lead compounds, where the alkyl groups, having been derived from ethylene, are multiples of two carbon atom chains. The TEL 10 mixture also normally contains scavengers such as ethylene dibromide (EDB) and ethylene dichloride (EDC). Other lead carriers known to those skilled in the art may also be utilized. Care should be taken to avoid excessive lead quantities since the lead 15 containing compounds, and combustion products, are toxic.

Manganese is added to yield up to 0.15 g Mn/gallon. Higher levels cause engine fouling. The 20 only compound used commercially at the present time as a source of manganese in gasoline is methylcyclopentyldienyl manganese tricarbonyl (MMT). While use of MMT in the United States has been restricted to leaded gasoline due to concerns that manganese, like lead, might foul catalytic converters, 25 MMT is used in combination with unleaded gasoline in Canada. It is therefore possible that the combination of alcohol and MMT might be useful in the production of higher octane unleaded gasoline. Other compounds which could be utilized in the present invention are 30 known to those skilled in the art, as are compounds which can be used in combination with MMT to reduce hydrocarbon emissions, as described in U.S. Patent Nos. 4,390,345, 4,317,657, 4,266,946, 4,191,536, and 4,175,927.

-8-

In general, 10% alcohol elevates the octane value of motor gasoline by 2 to 3, as a function of the starting octane: if the starting octane index is 84 or lower, an increase of 3 is obtained; if the 5 starting octane is about 87, an increase between about 2.0 and 2.5 is obtained; and, if the starting octane is 91 or greater, an increase of 2 or less is observed. As noted in the background of the invention, the increase provided by alcohol is lower 10 in the presence of lead. In the absence of alcohol, it has been demonstrated that 0.1 g Pb/gal increases the octane index by about 1. 0.1 g Mn/gal increases the octane index about 1 or more. The combination of 0.1 g Pb/gal and 0.1 g Mn/gal in gasoline in the 15 absence of alcohols increases the octane index by about 2 to 3.

On the basis of this information, one would predict that an unleaded gasoline having a starting octane of 85 would be required to produce a gasoline 20 mixture of 10% ethanol containing 0.1 g Pb/gal and 0.1 g Mn/gal and 90% unleaded gasoline having an octane index of approximately 89. It has been discovered that a gasoline having a starting octane value of between 83 and 84 is the maximum octane required to 25 produce a gasoline mixture having an octane of 89 or greater.

The present invention is further demonstrated by the following non-limiting examples. All percentages are by volume unless otherwise specified.

30 The advantage of the present invention over the use of either lead or alcohol to increase the octane of motor gasoline is demonstrated by these examples. The octane index was determined for the base gasoline composition. The mixture, containing gasoline,

-9-

oxygenated hydrocarbons, and organometallic compounds, was prepared and the octane value determined. The effect of the additives is illustrated by the difference between the two numbers.

5 Example 1. Comparison of Unleaded Gasoline containing Alcohol and Unleaded Gasoline containing Alcohol, Mn and Pb.

In this example, a gasoline with starting octane of $(R+M)/2 = 84.15$ is modified with either ethanol or 10 ethanol, tetraethyl lead (TEL) and methylcyclopentadienyl manganese tricarbonyl (MMT), to determine the effect of the addition of Pb and Mn to the alcohol. The results are shown in Table 1.

Table 1.

<u>Gasoline Sample</u>	<u>Research Octane (R)</u>	<u>Motor Octane (M)</u>	<u>(R + M) 2</u>
Unleaded Gasoline (UG)	88.3	80.0	84.15
UG + 10% Ethanol	92.4	82.3	87.35
UG + 10% Ethanol + 0.1 g Pb/gal + 0.1 g Mn/gal	95.7	84.1	89.9

From this data, the following table can be constructed whereby the blending octane value (BOV) of the blending agent into the gasoline is computed. Since the lead and manganese additives take no 5 appreciable volume, the combination of alcohol and organometallics is treated as a single component. The BOV is calculated from the known octane of the starting gasoline and the observed final octane of the blend, using the percentages of the components added. 10 The BOV is a predictive tool used for blenders to optimize compositions.

-10-

Table 2. BOV

<u>Blending Component</u>	<u>Observed BOV</u>	<u>Octane Increase</u>
10% Ethanol	116.2	3.2
10% Ethanol + 0.1 g Pb/gal		
+ 0.1 g Mn/gal	141.7	5.75

Thus, one can calculate that, for a target octane of 89.0 in the finished gasoline, the blender should start with a gasoline having an (R+M)/2 of 83.1.

$$0.9X + 0.1 (141.7) = 89.0$$

$$X = 83.1$$

Example 2. Comparison of the effect of methanol and ethanol mixtures on the increase in octane with Mn and Pb.

In this example, the effects of using ethanol versus ethanol-methanol mixtures, alone or in combination with Pb and Mn, were compared, as shown in Table 3.

Table 3.

<u>Gasoline Sample</u>	<u>Research Octane (R)</u>	<u>Motor Octane (M)</u>	<u>(R + M) 2</u>
Unleaded Gasoline (UG)	88.1	79.8	84.0
UG + 10% Ethanol	92.3	81.8	87.1
UG + 10% Ethanol + 0.1 g Pb/gal + 0.1 g Mn/gal	95.5	83.7	89.6
UG + 5% Methanol + 2.5 % Ethanol	91.6	81.1	86.4
UG + 5% Methanol + 2.5% Ethanol + 0.1 g Pb/gal + 0.1 g Mn/gal	94.3	82.8	88.6

-11-

Table 4. BOV for ethanol and methanol mixtures.

<u>Blending Component</u>	<u>Observed BOV</u>	<u>Octane Increase</u>
10% Ethanol	115.0	3.1
10% Ethanol + 0.1 g Pb/gal		
+ 0.1 g Mn/gal	140.0	5.6
5% Methanol + 2.5 % Ethanol	116.0	2.4
5% Methanol + 2.5% Ethanol 0.1 g Pb/gal + 0.1 g Mn/gal	145.3	4.6

Example 3. Comparison of the effect of Ethanol and Methanol on a higher octane unleaded gasoline.

In this example, a base gasoline having a fungible 87 octane index was used to compare the effect of 10% Ethanol, 5% Methanol + 2.5% Ethanol, and 0.1 g Pb/gal in combination with 0.1 g Mn/gal, as shown in Table 5.

Table 5.

<u>Gasoline Sample</u>	<u>Research Octane (R)</u>	<u>Motor Octane (M)</u>	<u>(R + M) / 2</u>
Unleaded Gasoline			
(UG)	92.2	82.5	87.35
UG + 10% Ethanol	95.2	83.9	89.55
UG + 10% Ethanol + 0.1 g Pb/gal + 0.1 g Mn/gal	97.6	85.5	91.55
UG + 5% Methanol + 2.5% Ethanol	94.8	83.2	89.0
UG + 5% Methanol + 2.5% Ethanol + 0.1 g Pb/gal + 0.1 g Mn/gal	96.7	85.1	90.9

-12-

Table 6. BOV Values for the higher octane unleaded gasoline mixtures.

<u>Blending Component</u>	<u>Observed BOV</u>	<u>Octane Increase</u>
10% Ethanol	109.4	2.2
10% Ethanol + 0.1 g Pb/gal		
+ 0.1 g Mn/gal	129.4	4.2
5% Methanol +		
2.5% Ethanol	109.4	1.65
5% Methanol + 2.5%		
Methanol + 0.1 g Pb/gal		
+ 0.1 g Mn/gal	134.7	3.55

The significance of the effect of combining the alcohol, manganese, and lead with the base gasoline is that, in contrast to the prior art, it allows the refiner to produce a base gasoline for manufacture of his leaded 89 octane grade gasoline which is one to two octane numbers lower than would have been expected; that is, the base gasoline need only be about 83 octane rather than an expected 85 octane. These saved octane numbers result in superior economics for the leaded grade and allow additional manufacture of higher octane, value added premium unleaded gasolines, especially for refiners who are octane short in their conventional petroleum refining configuration and do not want to invest in new crude oil processing equipment.

Modifications and variations of the present invention, a method and means for increasing the octane index of gasoline through the combination of short chain oxygenated hydrocarbons and organometallic compounds, particularly organolead and organomanganese compounds, will be obvious to those skilled in the art for the foregoing detailed description. Such modifications and variations are

-13-

intended to come within the scope of the appended claims.

-14-

We claim.

1. A gasoline mixture containing additives increasing the octane index of the base gasoline comprising between about 75-95% gasoline, 5 to 25% oxygenated hydrocarbons, 0.05 to 4 g Pb/gal. and 0.005 to 0.15 g Mn/gal.
2. The gasoline mixture of claim 1 wherein the oxygenated hydrocarbon is selected from the group consisting of methanol, ethanol, propanol, butanol, methyl tertiary-butyl ether, and tertiary-amyl methyl ether.
3. The gasoline mixture of claim 2 wherein the alcohol comprises about 33 to 100% ethanol and 0 to 67% methanol.
4. The gasoline mixture of claim 3 comprising between about 90 to 92.5% gasoline and 7.5 to 10% alcohol.
5. The gasoline composition of claim 1 comprising about 0.1 g Mn/gal. and 0.1 g Pb/gal.
6. The gasoline mixture of claim 1 wherein the manganese is an organomanganese compound.
7. The gasoline mixture of claim 6 wherein said organomanganese compound is methylcyclopentadienyl manganese tricarbonyl.

-15-

8. The gasoline mixture of claim 1 wherein the lead is an organolead compound.
9. The gasoline mixture of claim 8 wherein said organolead compound is a tetraalkyl lead compound.
10. A method for increasing the octane index of a gasoline mixture comprising
 adding an oxygenated hydrocarbon to gasoline to a final concentration by a volume of approximately 5 to 25%,
 adding between 0.005 g and 0.15 g Mn/gal of gasoline, and
 adding between 0.05 g and 4 g Pb/gal of gasoline.
11. The method of claim 10 further comprising selecting the oxygenated hydrocarbon from the group consisting of methanol, ethanol, propanol, butanol, methyl tertiary-butyl ether, and tertiary-amyl methyl ether.
12. The method of claim 11 comprising adding oxygenated hydrocarbons consisting of between 0-67% methanol and 33 to 100% ethanol to a volume of between about 7.5 to 10% of the gasoline mixture.
13. The method of claim 10 comprising adding Pb and Mn to a level of about 0.1 mg Pb/gal. gasoline and 0.1 mg Mn/gal. gasoline.

-16-

14. The method of claim 10 further comprising providing the Pb as an organolead compound.
15. The method of claim 14 further comprising selecting a tetraalkyl lead compound as the organolead compound.
16. The method of claim 10 further comprising providing the Mn as an organomanganese compound.
17. The method of claim 16 further comprising selecting methylcyclopentadienyl manganese tricarbonyl as the organomanganese compound.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/04257

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁸

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC4 C10L1/02, C10L1/10, C10L 1/14, C10L1/30
 U.S. CL. 44/56; 44/57; 44/68, 69;

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols			
US	44/56,	44/57,	44/68,	44/69

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	CA, A, 1,073,207, (DeJovine), 11 March 1980, All	1,2,45,79-11, 13,15 and 17
Y	US, A, 4,390,345, (Somorja), 28 June 1983, see col. 4.	1,2,4,5,7,9-11 13, 15 and 17
Y	US, A, 4,052,171, (Niebylski), 04 October 1977, see col. 4.	1,2,4,5,7,9-11 13, 15 and 17
Y	US, A, 4,028,065 (Sprague), 07 July 1977, see col. 3	1,2,4,5,7,9-11 13, 15 and 17
Y	EP, A, 0,121,089, (Majunke et al), 10 October 1984, All	1,2,4,5,7,9-11 13, 15 and 17
Y	EP, A, 3,330,165, (Majunke et al), 07 March 1985, All	1,2,4,5,7,9-11 13, 15 and 17

* Special categories of cited documents: ¹⁰

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

13 March 1988

Date of Mailing of this International Search Report

17 APR 1989

International Searching Authority

ISA/US

Signature of Authorized Officer

Margaret B. Medley
Margaret B. Medley

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4,376,636, (Weinberger), 15 March 1983	1,2,4,5,7,9-11 13, 15 and 17
A	US, A, 4,437,436, (Graiffe et al), 20 March 1984	1,2,4,5,7,9-11 13, 15 and 17
A	US, A, 3,869,262, (Mayerhoffer et al), 04 March 1975	1,2,4,5,7,9-11 13, 15 and 17
A	US, A, 4,141,693, (Feldman et al), 27 February 1979	1,2,4,5,7,9-11 13, 15 and 17
A	US, A, 4,067,699, (Lukasiewicz), 10 January 1978	1,2,4,5,7,9-11 13, 15 and 17
A	US, A, 3,950,145, (Niebylski), 13 April 1976	1,2,4,5,7,9-11 13, 15 and 17
Y	US, A, 3,030,195, (Ewan), 17 April 1962, All	1,2,4,5,7,9-11 13, 15 and 17
A	US, A, 2,365,009, (Robertson), 12 December 1944	1,2,4,5,7,9-11 13, 15 and 17